

What is corrosion?

By Doug Jones, expert team, Bossard Group

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What is corrosion?

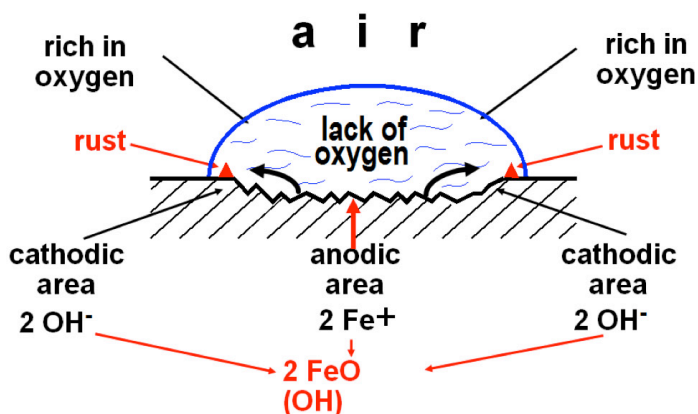
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In some cases corrosion can be seen as pleasing, such as a light patina on a copper watering can used for decoration, but most of time we like to prevent corrosion from taking hold of our designs until the expected life cycle of the product has passed.

Corrosion can lead to unhappy customers who may find rust stains on their shiny new garden tractor, or corrosion may even cause injury and death resulting from the collapse of a ceiling over a swimming pool who's roof was designed improperly. Understanding the types of corrosion and using good design practices to prevent it should be important to any engineer.

Principles of corrosion

The main cause of corrosion in fasteners is moisture and the electrochemical reactions that may occur between them and their mating components.



Water drop model

The figure above represents a water drop resting on a plain iron surface. The surface of the water droplet is exposed to air, making it rich in oxygen. The inside of the drop has a lack of oxygen, which creates a difference in electrochemical potential allowing electric current to flow. Electrical current flows through the water, which acts as an electrolyte, from the anodic surface of the iron to the cathodic surface of the water causing iron ions to dissolve.

At the same time, hydroxide ions are formed in the water and react with the iron ions causing the precipitation of iron hydroxide $\text{Fe}(\text{OH})_2$. The dissolved oxygen quickly oxidises this compound to form iron oxide hydrate $(\text{FeO}(\text{OH}))_n\text{H}_2\text{O}$, commonly referred to as rust.

It doesn't require much moisture for rust to begin. Corrosion starts at 60% relative humidity. If the air contains sulfur dioxide, hydrogen sulfide, nitrogen oxides, salt, ashes, soot and other pollutants, the chances of corrosion increase.

Types of corrosion

Uniform corrosion

Uniform corrosion of steel is the most common type of corrosion and is recognised by its reddish color distributed evenly through the exposed portion of the fastener. If left unattended, parts can become thinner and weaker eventually causing the joint to fail or become unable to disassemble.

Uniform corrosion prevention

- Protect parts from moisture.
- Use designs that allow for water run-off.
- Provide for good ventilation to allow drying.
- Keep surfaces clean and avoid contamination.
- Prevent continuous condensation.
- Protect fasteners with plating or coatings.

Crevice corrosion

Small gaps and recesses tend to draw in moisture and do not dry easily. Moisture in a crevice quickly loses oxygen and triggers anodic corrosion described in the water drop model. In the case of fasteners, the risk for crevice corrosion multiplies with the number of joint faces.

Austenitic stainless steel fasteners are also at risk for crevice corrosion, especially if used in an environment where chlorine ions are in the water.

Crevice corrosion prevention

- Minimise the use of washers – use flanged hardware.
- Make joint interfaces as smooth as possible.

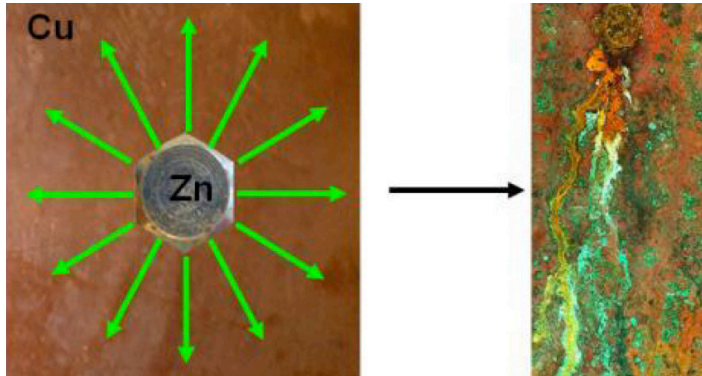
Galvanic corrosion

Joining together two dissimilar metals in the presence of moisture creates an electrochemical potential, which leads to corrosion. Current flows from the less noble, anodic metal to the more noble cathodic metal in this galvanic reaction, dissolving the less noble material.

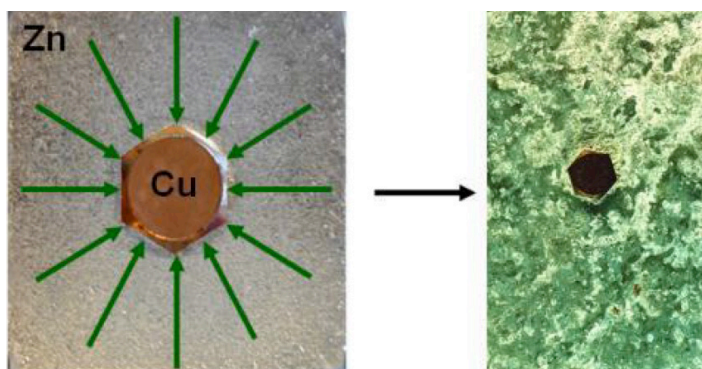
Electrochemical potentials of metal

water, pH 6,0	sea water, pH 7,5	
silver	silver	more noble (cathode)
copper	nickel	
nickel	copper	
stainless A2	stainless A2	
aluminum	steel	less noble (anode)
lead	cadmium	
tinn	aluminum	
lead	zinc	
steel	tin	
cadmium		
zinc		

The density of the corrosion current is directly proportional to the rate of the dissolving metal. In the case below, less noble zinc plated screw is used to attach a copper plate. The small surface area of the zinc compared to the much larger copper area creates a high current density. When moisture is added, the zinc quickly dissolves.



If we reverse the elements and attach a large piece of zinc plated steel with a copper fastener, the current density is very low, and the corrosion process is much more even between the two.



Galvanic corrosion prevention

- Fastener materials or protective finish should be either as noble or more noble than the joint members.
- Insulating plastic washers may be used for joints where clamp load is not critical.
- Stainless steel or copper parts should never be fastened with zinc plated fasteners

Pitting corrosion

On a metal surface that is coated by a very noble finish, such as nickel or chromium, pitting corrosion can occur. In the example below, the nickel plated steel had invisible pores, which allowed water through to the base metal. Crevice corrosion began underneath the surface, and showed through the pores as small dots or pits.



Stainless steel and aluminum alloys are also susceptible to pitting corrosion. These metals have a passive chromium oxide layer on the surface, which keeps them from corroding in a normal environment. If this passive layer is damaged locally, either mechanically or by solutions containing chloride ions, pitting corrosion may occur.

The exposed area becomes less noble than the much larger passivated area around it and creates a current density allowing for galvanic corrosion in the localised area, or pits. If oxygen is allowed to the active area, it may re-passivate, but dirt, salt deposits and chlorine residues can hamper the access of the oxygen making it difficult for the passive layer to reform.

Pitting corrosion prevention

- Talk to your nickel plater about subsequent treatments such as Castrol dewatering fluid (DW924) which fill pores.
- Keep surfaces clean and smooth.
- Avoid solid or liquid residues, especially chlorides – wash or rinse parts which have been exposed.
- Use A4 or 316 stainless steel containing molybdenum in environments subjected to chlorides.

Intergranular corrosion

Austenitic stainless steels (Cr Ni) may develop intergranular corrosion when heated to a high temperature for hot forming or welding. After heating (600°C – 900°C) and slow cooling, carbon can combine with chromium to form chromium carbides. Carbide formation depletes the chromium content, which is necessary to make the steel corrosion resistant. If the chromium level falls below 12%, corrosion may occur, especially in the grain boundaries.

Higher carbon content in the stainless steel and a slower rate of cooling will generate more carbides.

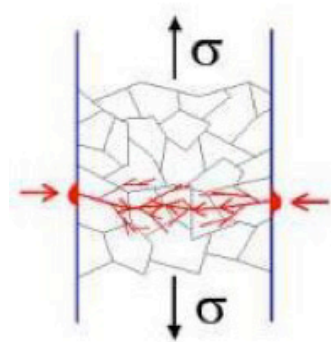
Intergranular corrosion prevention

- Use stainless steel with a carbon content below 0.05% if hot forming or welding.
- Quench parts in water directly after heating.
- Stainless steels containing over 0.05% carbon that will be subjected to high heat can be stabilised by adding titanium, niobium or tantalum (steels A3 and A5).

Stress corrosion cracking

Stress corrosion cracking may result when corrosion occurs on fasteners subjected to tensile stresses. Most often this type of failure starts with pitting corrosion.

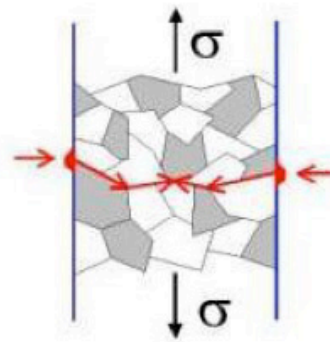
In the case of austenitic stainless steel that has suffered pitting corrosion in the presence of salt water, corrosion is accelerated perpendicular to the stress orientation and a crack is formed. Through the reactions that take place, red rust and hydrochloric acid are continuously formed at the base of the crack. The attack of the acid prevents repassivation, and the corrosion process continues, causing the crack to become deeper and deeper until the metal fails. Stress corrosion cracking may also occur in unalloyed and low alloy steels. The crack formed will be intergranular in nature while cracks in stainless austenitic steels will be transgranular.



Transgranular stress corrosion:

The growing crack runs through the grains and can form branches.

This is the crack formation in stainless austenitic Cr Ni steels.



Intergranular stress corrosion

The crack develops along the surfaces of the metal grains, i.e. along the grain boundaries.

Intergranular progression of cracks is more likely in unalloyed and low alloyed steels.

Stress corrosion cracking prevention

- Observe the prevention rules for pitting corrosion, especially in fasteners that are highly stressed.
- Periodically inspect safety critical parts for any signs of corrosion.
- Consider hot dip galvanising for safety critical parts, making corrosion noticeable.
- Ensure that safety critical fasteners are accessible for inspection and replacement.

Hydrogen embrittlement

Hydrogen may be induced into steel during acid cleaning or electroplating. During processing, most hydrogen escapes in the form of gas, but some of it diffuses the metal in atomic form. Hydrogen atoms stay highly mobile in the metal's grain structure, and have a tendency to migrate to areas of stress concentration.

When high strength fasteners (hardness > 320 HV) are stressed, small surface defects such as scratches or inclusions may open up in the form of a very small crack. If hydrogen is present in the steel, atoms are attracted by the tensile stresses around the tip of the crack and form a 'hydrogen atom cloud' there. The hydrogen weakens the microstructure of the metal and the crack may continue to grow until the part fails.

Hydrogen embrittlement failure will always be a delayed failure, not occurring at the time of assembly, but hours to weeks later. Typical failures occur within 24 – 48 hours. The most susceptible parts are threaded fasteners of metric property class 10.9 or higher, imperial grade 8 or higher. Also at risk are case hardened, threaded parts such as thread forming screws or serrated screws, and anything made of spring steel such as lock washers and retaining rings.

For high strength parts that are electroplated, a baking process may be done for a minimum of four hours at 200°C – 230°C within four hours of plating in an effort to drive out the hydrogen. Although this practice is highly recommended and widely used, it is no guarantee that the risk has been eliminated. The best practice is not to introduce hydrogen into the parts in the first place.

Other coatings that do not create hydrogen should be considered for high strength fasteners.

Three things are key for hydrogen embrittlement:

1. A susceptible material – steel with a hardness of > 320 HV or a tensile strength >1000N/mm.
2. A process that introduces hydrogen into the metal.
3. A sustained tensile stress.

If any of the three things above are removed from the equation, hydrogen embrittlement will not be a concern. That means that property class 8.8 or grade 5 bolts are not at risk, and neither are fasteners finished with a coating that does not introduce hydrogen.

It should also be noted that the corrosion process produces hydrogen, so high strength fasteners should be protected from corrosion as well. Delayed failures that occur many weeks or months after assembly are normally the result of corrosion induced hydrogen rather than from a hydrogen source introduced during the processing of the parts.

Hydrogen embrittlement prevention

- Do not electroplate or use acid cleaning for high strength fasteners with a hardness of > 320 HV or a tensile strength >1000N/mm.
- If electroplating is unavoidable, make sure the parts are clean as possible to minimise the time needed for acid cleaning and follow the baking process described above.

Summary

Keep in mind that when designing products, fasteners are an integrated part of the entire assembly and cannot be treated as separate entities. Fasteners must always be as good or better than the parts they hold together. By understanding the different types of corrosion and the preventive measures and following the rules below, good, long lasting joints can be achieved:

1. Joining elements should always be as good or even better than the joined parts.
2. Fastened joints should never become points of weakness.
3. Make sure that all fastened joints, especially critical ones, are accessible for inspection and replacement. ■